



Catalytic conversion of tar from hot coke oven gas using 1-methylnaphthalene as a tar model compound

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ABSTRACT

High concentration (1.3 vol.%) of 1-methylnaphthalene was selected as a tar model compound to investigate the catalytic conversion of tar from hot coke oven gas (COG) with lower steam content under atmospheric pressure over the Ni/MgO/Al₂O₃ catalysts. The catalysts were prepared by impregnating boehmite (AlOOH) with an aqueous solution of magnesium nitrate and nickel nitrate. The effects of Ni loading, reaction temperature, steam/carbon (S/C) molar ratio on the catalytic performance of the catalysts were discussed in detail. The catalysts exhibited excellent activity, stability and resistance to carbon deposition. Tar compounds could be completely converted into light fuel gases over 10% Ni/MgO/Al₂O₃ at 775 °C and S/C = 0.7. The effect experiments of sulphur were performed by adding 1000 and 2500 ppm H₂S in the feed. The used catalysts were characterized by XRD and TG analyses. It was first found that addition of H₂S in the feed could greatly inhibit the carbon formation on the catalyst surface and lead to significant improvement in the activity and stability of the catalyst. This phenomenon has never been reported previously in the tar steam reforming.

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1. Introduction

Hydrogen has been considered as the most promising energy carrier because of its highly efficient and non-polluting characters [1–3]. Tremendous efforts are being undertaken to develop new technologies and reduce the cost of hydrogen production. At present, hydrogen was produced mainly through the steam reforming or the partial oxidation of natural gas [4–6]. As one of the options, a large amount of the concomitant coke oven gas (COG) in the coke making process, in which there are abundant H₂ and CH₄, the volume fraction of which are ca. 55% and ca. 25%, respectively, is a potential source for low cost hydrogen production. This hydrogen production pathway can achieve the benefits of energy and greenhouse gas emission reduction [7]. Some iron plants currently use pressure swing adsorption (PSA) to acquire hydrogen from cold clean COG. However, the economy of this process can be improved through recovering more hydrogen from COG in the future [8]. There have been some reports of hydrogen production from COG by reforming of methane in the past years [9,10].

Hot COG emitted from coke ovens at a high temperature between 750 and 850 °C contains ca. 100 g m^{−3} of tar like benzene (C₆H₆) and naphthalene (C₁₀H₈) and hundreds of ppm sulphide. These compounds have to be cooled and removed with an ammonia

aqueous solution spray for preventing coke deposition and sulphur poisoning of the catalysts. This process causes not only substantial loss of heat but also some tar loss in water, which leads to serious secondary pollution. The economic way is to convert tar components into small gas molecules through the catalytic hydrocracking or reforming reactions directly using the sensible heat and chemical energy in hot COG instead of a separation [11].

Ni/γ-Al₂O₃ catalysts have been widely investigated because of low cost and good catalytic activity for hydrocracking of heavy hydrocarbons and catalytic cracking of biomass tar. However, carbon deposition and sintering of active Ni component at high temperature caused deactivation of the catalysts [12–14]. In addition, Ni catalysts were usually poisoned by sulphur compounds due to the strong adsorption on the active sites [15,16]. Compared with biomass gasification system, hot COG contains only 10–15 vol.% water, which helps drive the steam reforming reaction to substantial completion and inhibit coke formation, and the steam/carbon (S/C) molar ratio is very low. Conventional Ni/γ-Al₂O₃ catalysts for biomass tar conversion will be deactivated immediately due to carbon deposition, leading to bed clogging. Up to now, there are only a few of reports on catalytic conversion of tar compounds into light fuel gases in hot COG [17–21]. It has been reported that alkaline earth oxides MgO could improve the surface properties of the Ni catalysts and enhance their reaction performance, resistance to carbon deposition and tolerance to sulphur [22–26].

In this paper, Ni/MgO/Al₂O₃ catalysts were used to investigate the catalytic conversion of 1-methylnaphthalene (C₁₁H₁₀)

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as a model tar compound in hot H₂-rich COG. The reason of 1-methylnaphthalene as the model compound is that it can be cracked into benzene and naphthalene, which actually exists in tar and represents the characters of the tar. So the conversion procedure is closer to that of practical tar. It was first found that the Ni/MgO/Al₂O₃ catalysts could not only have high activity and resistance to carbon deposition, but favor the conversion of tar at high concentrations of H₂S as well.

2. Experimental

2.1. Catalyst preparation

Ni/MgO/Al₂O₃ catalysts were prepared via impregnating boehmite (AlOOH) powder with an aqueous solution of magnesium nitrate (≥99.0%, Sinopharm Chemical Reagent Co., Ltd.) and nickel nitrate (≥99.0%, Sinopharm Chemical Reagent Co., Ltd.). Boehmite was obtained by calcining SB pseudoboehmite powder (from Condea, Germany) at 500 °C for 10 h with a heating rate of 1 °C min⁻¹. In a typical procedure, 10 g of boehmite was added under stirring into 50 mL of an aqueous solution of magnesium nitrate and nickel nitrate with an MgO/Al₂O₃ mass ratio of 1:5 and Ni content varying from 0 to 15 wt.% and kept at room temperature for 2 h. The mixture was evaporated out at 80 °C and then was dried at 110 °C overnight, and finally the solid was calcined at 800 °C for 10 h.

2.2. Catalyst characterization

N₂ adsorption was carried out using a Micromeritics ASAP 2020 Sorptometer at liquid nitrogen temperature. Before the measurements, the samples were degassed at 300 °C for 6 h. The specific surface areas were evaluated using the Brunauer–Emmett–Teller (BET) method in the P/P_0 range of 0.05–0.3. Power X-ray diffraction (XRD) was performed on a Rigaku D/Max-2550 apparatus using Cu Kα radiation at 40 kV and 200 mA. Thermogravimetric (TG) analyses were carried out on a SDT Q600 thermogravimetric analyzer with a heating speed of 10 °C min⁻¹ in an air flow of 30 mL min⁻¹.

2.3. Catalytic tests and analysis

The catalytic tests were carried out at atmospheric pressure in a continuous flow fixed-bed quartz tube reactor with an internal diameter of 10 mm and a length of 1000 mm. Water and 1-methylnaphthalene were pumped via two dual micro-plunger pumps, respectively, through a preheater with a set temperature of 350 °C, and then into the reactor. The temperature of the catalyst was monitored using a thermocouple placed in the middle of the catalyst bed. 1 g of the catalyst with particle sizes of 20–40 mesh was placed at the middle portion of the reactor. Prior to testing, the catalyst was first reduced in a flow of 15 vol.% H₂/N₂ (30 mL min⁻¹) by increasing the temperature to 650 °C at a heating rate of 10 °C min⁻¹, followed by at a rate of 1 °C min⁻¹ from 650 to 800 °C, and finally kept at 800 °C for 8 h. After that, the reactant gas consisting of a mixture of steam and H₂ was introduced to the reaction system with a constant concentration of 1.3 vol.% (82.4 g m⁻³) 1-methylnaphthalene in the feed gas, which is close to practical tar content in hot COG, at a space velocity (SV) of inlet gas of 1500 mL g_{cat}⁻¹ h⁻¹. The sulphur effect experiments were performed by introducing small amounts of H₂S to the feed gas. To avoid the condensation of the liquids, the pipe line was kept at a temperature of 250 °C.

After the 2 h reaction, the reaction system became stable and the products were sampled at appropriate reaction intervals with a six-way valve and analyzed using an on-line GC-FID gas chromatograph with a CP-sil 5 CB column for benzene, naphthalene and

1-methylnaphthalene, followed by another GC-TCD gas chromatograph with a packed sieve column for H₂, CH₄, CO and a Porapak Q column for CO₂ in the cooled, purified gas mixture. The flow rate of the exit gas was measured by a soap flow meter.

1-Methylnaphthalene conversion and the yields of the products formed were calculated with the formulae (Eqs. (1)–(4)) shown as follows.

1-Methylnaphthalene conversion, noted X_M (Eq. (1)), is defined as the ratio of the molar amount of 1-methylnaphthalene consumed to the molar amount of 1-methylnaphthalene in the feed gas:

$$X_M = \frac{F_{(M,in)} - F_{(M,out)}}{F_{(M,in)}} \times 100\% \quad (1)$$

$F_{(M,in)}$ and $F_{(M,out)}$: 1-methylnaphthalene molar flow rate of the inlet and outlet gases.

Yields of carbon-containing products (CH₄, CO and CO₂), noted Y_i (Eq. (2)), are defined as the percentage of the molar amount of carbon in the product i to the molar amount of carbon in 1-methylnaphthalene in the feed gas:

$$Y_i = \frac{F_{(i,out)}}{11F_{(M,in)}} \times 100\% \quad (2)$$

$F_{(i,out)}$: molar flow rate i = CO, CO₂, CH₄.

Benzene yield, noted Y_B (Eq. (3)), is expressed as the percentage of the molar amount of carbon in benzene in the exit gas to the molar amount of carbon in the feed gas:

$$Y_B = \frac{6F_{(B,out)}}{11F_{(M,in)}} \times 100\% \quad (3)$$

F_B : molar flow rate of benzene.

Naphthalene yield, noted Y_N , is calculated by Eq. (4):

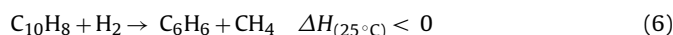
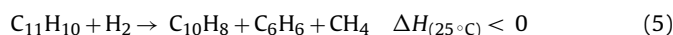
$$Y_N = \frac{10F_{(N,out)}}{11F_{(M,in)}} \times 100\% \quad (4)$$

F_N : molar flow rate of naphthalene.

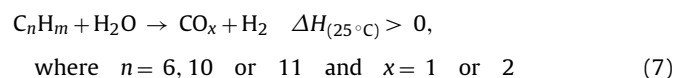
3. Results and discussion

It is well known that tar reforming is rather complex and many parallel and consecutive reactions can take place during the catalytic conversion of tar at high temperature. The distribution of the final products has a strong dependence on the nature of catalysts, operation parameters, steam/carbon molar ratios, etc. [27,28]. The reaction process of 1-methylnaphthalene in the presence of water and excess hydrogen at high temperature mainly contains the reactions as follows:

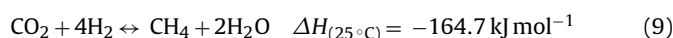
Hydrocracking (Eqs. (5) and (6)):



Steam reforming (Eq. (7)):



Methanation (Eqs. (8) and (9))



Water–gas shift (Eq. (10)):



Table 1

Reaction results of 1-methylnaphthalene and carbon balances over the Ni/MgO/Al₂O₃ catalysts with different Ni contents after 4 h reaction.

Ni content (wt.%)	X_M (%)	Yield (%)					C_b (%)
		C ₁₀ H ₈	C ₆ H ₆	CO	CH ₄	CO ₂	
No catalyst	100	91.1	1.0	7.5	0	0	99.8
0	100	82.3	2.5	8.1	5.2	1.0	98.5
2	100	30.9	7.5	38.5	20.2	1.2	97.9
6	100	1.8	14.2	52.6	27.8	1.2	97.8
10	100	0	0	63.5	33.1	1.1	98.1
15	100	0	0	60.3	37.2	0.9	98.2

Reaction conditions: H₂, 88.7 vol.%; C₁₁H₁₀, 1.3 vol.%; S/C, 0.7; reaction temperature, 775 °C.

Other reactions also have to be taken into account in the reaction process such as carbon formation by decomposition and cracking of 1-methylnaphthalene. The carbon balance (C_b), which is defined as the percentage of the total molar amount of carbon in the exit gas to the total molar amount of carbon in the inlet gas during the given reaction time, is used to estimate the deposited carbon over the catalyst.

3.1. Nickel content effect

Blank experiments were performed using silicon carbide as the bed material to check the possible thermal or wall reactions (Eqs. (5) and (6)) using a gas mixture of steam and H₂ with 1.3 vol.% 1-methylnaphthalene and S/C=0.7 in the feed in the range of 700–800 °C. It was found that 1-methylnaphthalene was fully converted into naphthalene, benzene and CO. Table 1 shows that their yields at 775 °C after 4 h reaction were 91.1%, 1.0% and 7.5%, respectively. There was no CH₄ detected in the exit gas. This was likely due to the easier reaction of the methyl radical intermediates in the thermal reaction process with the steam. After the reaction, no carbon deposition was observed on silicon carbide and the wall of the reactor.

The reaction results of 1-methylnaphthalene after 4 h of time on stream over the Ni/MgO/Al₂O₃ catalysts with Ni content varying from 0 to 15% at 775 °C and S/C=0.7 are given in Table 1. All the Ni/MgO/Al₂O₃ catalysts showed 100% conversion of 1-methylnaphthalene. The yield of naphthalene rapidly decreased with the rise in Ni content, and in the meanwhile, the yield of benzene displayed a contrary trend and increased from 2.5 to 14.2% with increasing Ni content up to 6%. This implied that benzene was an intermediate compound in the catalytic reforming of naphthalene to light gases. When the Ni content was enhanced up to 10%, both naphthalene and benzene disappeared in the exit gas, while the yields of CO and CH₄ were increased from 8.1 and 5.2% to 63.5 and 33.1%, respectively. These results indicated that nickel atoms were active sites both for the catalytic steam reforming of tar (Eq. (7)) and for the methanation reaction of CO_x and H₂ (Eqs. (8) and (9)). With the tar compounds exhausted in the reaction system, the methanation reaction continued to proceed with the increased Ni content. When Ni content reached 15%, the CO yield decreased to 60.3% and the CH₄ yield formed increased to 37.2%, which were very close to the theoretical values (Y_{CO} , 59.8%; Y_{CH_4} , 39.3%; Y_{CO_2} , 0.90%) in the equilibrated system at the operation conditions. For all of these Ni/MgO/Al₂O₃ catalysts, the CO₂ yields were relatively lower, but more than the equilibrium value. This implied that the CO₂ formation might be mainly responsible for the steam reforming of tar rather than the water gas shift reaction (Eq. (10)). The carbon balances in Table 1 were more than 97.5%, suggesting that the Ni/MgO/Al₂O₃ catalysts possessed excellent resistance to carbon deposition.

Table 2

Reaction results of 1-methylnaphthalene and carbon balances over the 10% Ni/MgO/Al₂O₃ catalyst at different temperatures after 4 h reaction.^a

Temperature (°C)	X_M (%)	Yield (%)					C_b (%)
		C ₁₀ H ₈	C ₆ H ₆	CO	CH ₄	CO ₂	
700	100	12.1	9.4	38.5 (34.1)	35.1 (41.7)	3.7 (2.7)	97.8
750	100	4.9	4.5	53.1 (52.3)	33.9 (36.8)	2.0 (1.5)	98.2
775	100	0	0	63.5 (59.8)	33.1 (39.3)	1.1 (0.9)	98.1
800	100	0	0	64.0 (63.3)	29.5 (36.1)	0.6 (0.6)	95.5

Reaction conditions: H₂, 88.7 vol.%; C₁₁H₁₀, 1.3 vol.%; S/C, 0.7.

^a The values in parentheses are the equilibrium values on the basis of the total small gas molecules (CO, CH₄, H₂, CO₂ and H₂O) except naphthalene and benzene.

3.2. Effect of reaction temperature

The effect of the reaction temperature on the performance of the 10% Ni/MgO/Al₂O₃ catalyst for the conversion of 1-methylnaphthalene at S/C=0.70 is listed in Table 2. 1-methylnaphthalene was completely converted in the range of 700–800 °C. The yields of naphthalene and benzene decreased from 12.1 and 9.4% to zero with elevating the reaction temperature from 700 to 775 °C, respectively. This indicated that higher temperature favored the conversion of tar into light gas molecules, which was consistent with the endothermic nature of the steam reforming of hydrocarbon. The thermodynamic equilibrium analysis showed that the yields of naphthalene and benzene should be zero when the reaction system reached chemical equilibrium between 700 and 800 °C. This implied that the catalytic reforming of naphthalene and benzene were governed by reaction kinetics below 775 °C. The CO yield increased with the rise in temperature, while the CH₄ yield decreased.

The comparison between the experimental results and the equilibrium values (Table 2) estimated on the basis of the total small gas molecules (CO, CH₄, H₂, CO₂ and H₂O) except naphthalene and benzene showed that the CH₄ yields were below the theoretical values, implying that its formation process was controlled by the kinetics. The yields of CO and CO₂ were higher than the corresponding equilibrium values, suggesting that they were both mainly responsible for the steam reforming of tar (Eq. (7)). When the reaction temperature was above 750 °C, both of them were closer to the equilibrium values. This indicated that the reaction rate of CO_x and H₂ (Eqs. (8) and (9)) increased with the rise in reaction temperature. The CO yields increased with the rise in temperature, while the CO₂ yields decreased, demonstrating that higher temperature was more favorable to the steam reforming of tar to CO and H₂ in the two parallel tar reforming reactions (Eq. (7)), which was in accordance with the thermodynamic properties. The carbon balances were more than 97.5% in the range of 700–775 °C, while the value at 800 °C was only 95.5%. This might be because tar compounds suffered thermal cracking at higher temperature, leading to more coke accumulation over the catalyst surface.

3.3. Effect of S/C ratio

In the steam reforming of biomass tar, the S/C molar ratio had great influence on the catalytic performance. Generally the steam reforming of tar was investigated in the S/C molar ratio range of 1–9 due to the coke formation under atmospheric pressure. However, it was found that the reforming of 1-methylnaphthalene was stable under lower S/C ratio over the Ni/MgO/Al₂O₃ catalyst, and showed excellent catalytic performance due to the presence of excessive hydrogen in COG.

The catalytic reaction of 1-methylnaphthalene was first conducted over the 10% Ni/MgO/Al₂O₃ catalyst without steam in the feed at 775 °C. It could be seen that 1-methylnaphthalene was

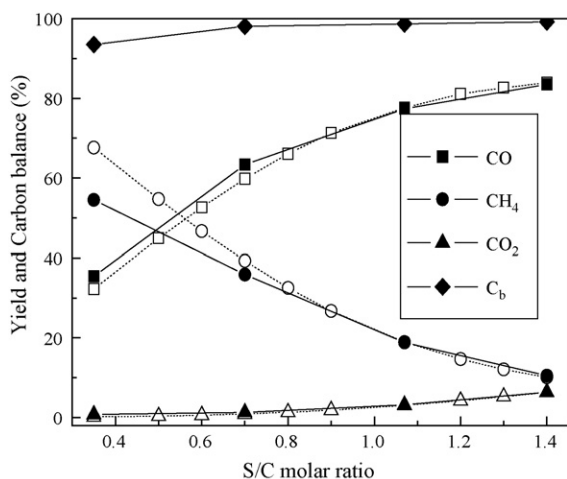


Fig. 1. Effect of S/C molar ratio on the yields of the products (solid line, solid symbol), the estimated equilibrium values (dot line, hollow symbol) and the carbon balances over the 10% Ni/MgO/Al₂O₃ catalyst. Reaction conditions: (H₂ + H₂O), 98.7 vol.%; C₁₁H₁₀, 1.3 vol.%; reaction temperature, 775 °C; reaction time, 4 h.

mainly hydrocracked to naphthalene, benzene and CH₄, and the catalyst was rapidly deactivated due to coke deposition. So the effect of the S/C ratio on the catalytic performance was studied in the S/C molar ratio range of 0.35–1.4. There were no tar components like 1-methylnaphthalene, naphthalene and benzene observed in the exit gas. The yields of CO, CH₄ and CO₂ at different S/C molar ratios are presented in Fig. 1. It was found that the S/C molar ratio had a significant influence on the product yields. The yields of CO and CO₂ increased with raising the S/C molar ratio, while the yield of CH₄ decreased with the S/C ratio. This indicated that increasing the steam content in the feed could promote the catalytic steam reforming reactions of tar compounds (Eq. (7)), and inhibit the methanation of CO_x (Eqs. (8) and (9)).

The experimental results were compared with the thermodynamic equilibrium values shown in Fig. 1. It could be seen that the yields of CO and CO₂ were higher than the equilibrium values, while the yield of CH₄ was lower than the equilibrium ones when the S/C molar ratio was below 1.1. When the S/C molar ratio was elevated, the difference between these two-group data curves became smaller, and finally showed a complete agreement in the range of 1.1–1.4. This indicated that the higher S/C molar ratio could accelerate the methanation rate of CO_x towards the system equilibrium. The carbon balance at S/C = 0.35 (Fig. 1) was 93.5%, implying there was higher carbon deposition during the reaction process, while the carbon balances in the S/C range of 0.7–1.4 were above 97.5%.

3.4. Effect of H₂S in the feed on catalytic activity

Ni-based catalysts have been considered to be active and promising for the hydrocracking and the methanation of tar. However, the non-modified Ni-based catalysts were easily poisoned by sulphur in the reaction [15]. In practice, there are always sulphur compounds varying from 500 to 3000 ppm in hot COG. So the sulphur tolerance of the catalysts has been a key for the newly developed catalysts to be successfully applied for the direct catalytic conversion of tar in hot COG. In order to examine the effect of sulphur on the catalyst performance, 1000 and 2500 ppm of H₂S were added in the reactant mixture, respectively. Fig. 2 shows the effect of H₂S on the yields of naphthalene and benzene as a function of the reaction time over the 10% Ni/MgO/Al₂O₃ catalyst at 775 °C. It could be seen that H₂S concentration had no influence on the conversion of 1-methylnaphthalene, which was kept at 100% (not shown), but caused substantial changes in the yields of naphtha-

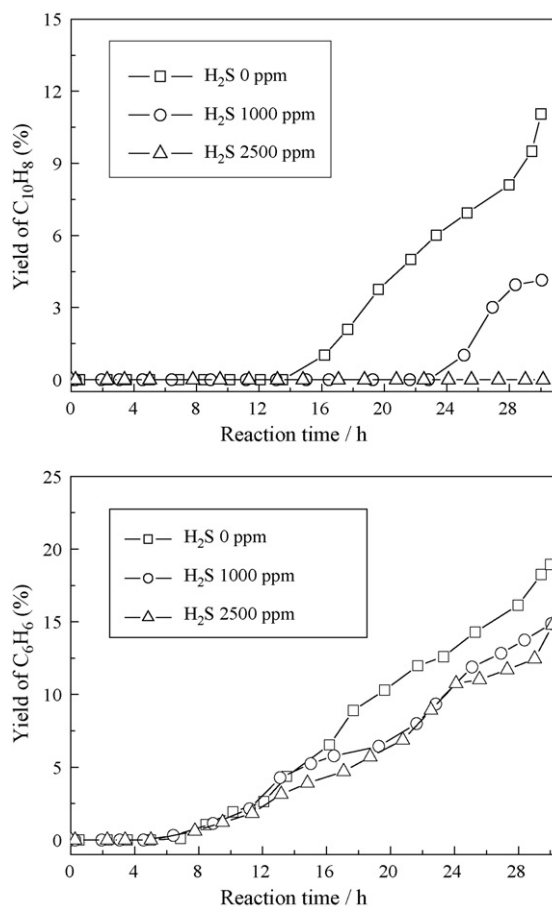


Fig. 2. Effect of different concentration H₂S on the yields of naphthalene and benzene over the 10% Ni/MgO/Al₂O₃ catalyst. Reaction conditions: (H₂ + H₂S), 88.7 vol.%; C₁₁H₁₀, 1.3 vol.%; S/C, 0.7; reaction temperature, 775 °C.

lene and benzene during the reaction period of 30 h. In the absence of H₂S, naphthalene appeared in the exit gas after 14 h reaction time on stream, and its yield increased up to 11.0% with prolonging the reaction time to 30 h. When the concentration of H₂S was 1000 ppm, naphthalene was observed in the exit gas after 23 h reaction time on stream, and its yield was 4.1% at 30 h reaction time. As the H₂S concentration was further raised to 2500 ppm, naphthalene was not found in the whole reaction process. Benzene could be detected after ca. 5 h time on stream at different H₂S concentrations, but the benzene yield in the absence of H₂S was higher than those in the presence of H₂S. These results indicated that addition of H₂S could promote the steam reforming of tar compounds in H₂-rich COG. It is noticeable that this phenomenon has never been reported previously in the tar steam reforming. The carbon balances (C_b) estimated by the total amount of carbon in the exit gases in Table 3 showed an obvious increase with the rise in H₂S con-

Table 3

Deposited carbon and carbon balances over the 10% Ni/MgO/Al₂O₃ catalyst for the conversion of 1-methylnaphthalene for 30 h at different H₂S concentrations.

H ₂ S concentration (ppm)	Carbon amount by TG (mg g _{cat} ⁻¹)	P _{carbon} ^a (%)	C _b (%)
0	258	7.5	92.5
1000	156	4.5	94.9
2500	38	1.1	98.8

Reaction conditions: (H₂ + H₂S), 88.7 vol.%; C₁₁H₁₀, 1.3 vol.%; reaction temperature, 775 °C.

^a The percentage of the deposited carbon determined by TG to the total carbon in the feed.

Table 4

BET surface areas, pore volumes and pore sizes of the Ni/MgO/Al₂O₃ catalysts with different Ni loadings calcined at 800 for 10 h.

Ni loading (wt.%)	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore diameter (nm)
0	82.3	0.20	9.5
2	78.0	0.20	10.0
6	73.1	0.20	10.9
10	61.2	0.18	11.7
15	59.9	0.16	10.8

tent, suggesting the reduction of the deposited amount of carbon at high H₂S concentration. However, the C_b value in the absence of H₂S after 30 h reaction was lower than that after 4 h reaction (Table 1). This implied the rate of the coke deposition increased with prolonging reaction time.

It has been known that the deactivation of Ni-based catalysts was mainly caused by the surface coverage of inert carbon on metallic nickel for the reforming reaction of hydrocarbon [12,13]. The coke formation had a strong dependence on the nature of Ni particles [29]. Higher synergetic Ni active sites favored the formation of the carbide carbon (*C), which was a precursor of the graphitic carbon that causes deactivation [29,30]. In the presence of H₂S, sulphur could adsorb on the active Ni sites as presented in Eq. (11), at which the reaction was reversible at high temperature [31]. This process could prevent CH_x (1 ≤ x ≤ 3) from occupying the proper active sites to form *C, leading to the reduction of carbon deposited on the catalyst surface, as shown in TG profiles (see Fig. 4). As a result, the activity and stability of the catalyst were improved for the conversion of naphthalene and benzene to light fuel gases.



3.5. Characterization of catalysts

The BET surface areas, pore volumes and pore diameters of the Ni/MgO/Al₂O₃ catalysts are listed in Table 4. The catalysts possessed smaller specific surface areas, pore volumes and pore diameters than those (156.7 m² g⁻¹, 0.49 cm³ g⁻¹ and 12.5 nm) of the Al₂O₃ support calcined at 800 °C. This was attributed to the blocking of part of pores in the support and the formation of Mg(Ni)Al₂O₄ on the surface of the catalysts [32]. The specific surface area and pore volume of the catalysts gradually decreased with the increased Ni loading, while the average pore diameter had no obvious change.

Fig. 3 shows the XRD patterns of the Al₂O₃ support and the 10% Ni/MgO/Al₂O₃ catalyst obtained under different conditions. The Al₂O₃ powder, which was prepared via calcining SB pseudobochmite at 500 °C for 10 h, was seen to consist of boehmite (AlOOH) phase (Fig. 3(a)). The Ni/MgO/Al₂O₃ catalyst calcined at 800 °C for 10 h showed three strong diffraction peaks at 2θ = 36.76°, 45.08° and 65.32° corresponding to the MgAl₂O₄ or NiAl₂O₄ spinels, which were indistinguishable in the XRD patterns [33,34]. No characteristic peaks corresponding to the NiO phase was observed, demonstrating that there was no free NiO species on the catalyst. After reduced in a flow of 15% H₂/N₂ at 800 °C for 8 h, the catalyst showed three new peaks at 2θ = 44.43°, 51.56° and 76.32° corresponding to Ni(1 1 1), (2 0 0) and (2 2 0) reflections, respectively. This showed that Ni²⁺ ions in the sample were reduced to metal Ni [35]. The diffraction peaks were weak and the peak shapes were relatively diffused, implying that the Ni particles formed were smaller and highly dispersed on the catalyst surface. The apparent crystallite size estimated from broadening of the Ni(2 0 0) reflection using the Scherrer formula [36] was ca. 8.2 nm.

The XRD patterns of the 10% Ni/MgO/Al₂O₃ catalyst after the catalytic reaction of 1-methylnaphthalene with different H₂S con-

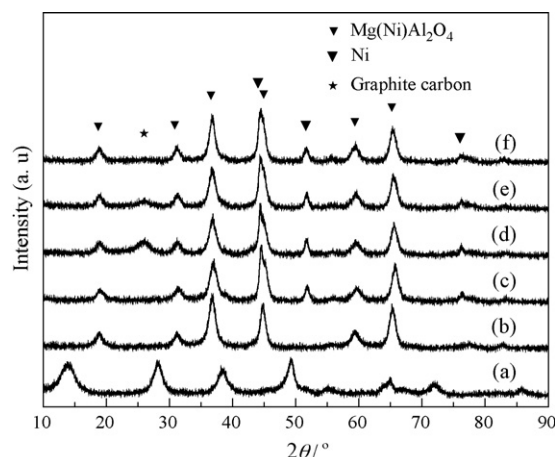


Fig. 3. XRD patterns of the catalysts. (a) SB powder calcined at 500 °C; (b) 10% Ni/MgO/Al₂O₃ calcined at 800 °C; (c) 10% Ni/MgO/Al₂O₃ reduced at 800 °C for 8 h; (d) 10% Ni/MgO/Al₂O₃ at 775 °C after 30 h reaction in the absence of H₂S; (e) 10% Ni/MgO/Al₂O₃ after 30 h reaction at 775 °C in the presence of 1000 ppm H₂S; (f) 10% Ni/MgO/Al₂O₃ after 30 h reaction at 775 °C in the presence of 2500 ppm H₂S.

centrations in the feed gas at 775 °C for 30 h are illustrated in Fig. 3(d)–(f). The diffraction peaks of the Mg(Ni)Al₂O₄ phase and metallic Ni had little change compared to those before the reaction. This demonstrated that the catalyst possessed stable structure and the Ni particle sizes were unchanged in the reaction process. After the catalytic reaction, a weak diffraction peak at 26.2° was observed, which was attributed to graphitic carbon (PDF 26-1080), which was mainly responsible for the deactivation of Ni-based catalysts in the reforming of hydrocarbons [30]. It could be found that the intensity of the carbon peaks greatly decreased with the increase in H₂S concentration. When H₂S content in the feed gas rose to 2500 ppm, the carbon peak disappeared. This indicated that the presence of H₂S in the feed inhibited the coke formation on the catalyst surface, leading to significant improvement in the activity and stability of the catalyst for the conversion of tar in agreement with the results in Fig. 2.

The carbon deposition on the used catalyst was investigated by TG analysis in air and the results are shown in Fig. 4. All the catalysts showed first weight loss of 1–2% at temperature lower than 350 °C corresponding to the desorption of physically adsorbed water. This was followed by a small weight augment in the range of 350–500 °C, assigned to the Ni metal oxidation in the catalyst, and

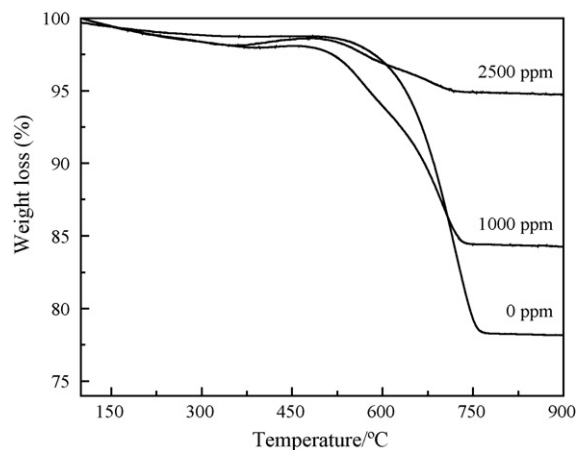


Fig. 4. TG profiles of the 10% Ni/MgO/Al₂O₃ catalyst for the catalytic conversion of 1-methylnaphthalene at 775 °C and S/C = 0.7 for 30 h with different H₂S concentrations in the feed.

subsequent large weight loss was attributed to the removal of the deposited carbon. Obviously, the amount of carbon on the used catalyst had a substantial decrease with increasing H_2S concentration up to 2500 ppm, which was in accordance with the results displayed in Fig. 3. Table 3 gives the amount of carbon estimated from 500 to 800 °C in the profiles. It could be found that the deposited amount of carbon was dramatically reduced from 258 to 38 mg $\text{g}_{\text{cat}}^{-1}$ when H_2S concentration was enhanced from 0 to 2500 ppm. Correspondingly, the percentage of the deposited carbon to the total carbon in the feed decreased from 7.5 to 1.1%, which was very close to those on basis of the total carbon in the exit gas.

4. Conclusions

The Ni/MgO/ Al_2O_3 catalysts which were prepared by impregnating boehmite (AlOOH) with an aqueous solution of magnesium nitrate and nickel nitrate exhibited excellent activity, stability and resistance to carbon deposition for the catalytic conversion of tar in H_2 -rich hot COG. Ni loading, reaction temperature, S/C molar ratio had significant effect on the conversion of tar and the distribution of the product gases. Tar compounds could be completely converted into light fuel gases over the 10%Ni/MgO/ Al_2O_3 catalyst at low S/C molar ratio. The presence of H_2S in the feed could greatly inhibit the carbon formation on the catalyst surface and improved the activity and stability of the Ni/MgO/ Al_2O_3 catalyst for the reforming reaction of tar.

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